

FINAL  
7N-27-12  
0011

**FINAL REPORT**  
**Photochemically and Thermally Cross-linkable Polyconjugated Systems**

Project Starting Date: April 1, 1995 (NAG 10-0156)

Summary of work done for April 1, 1995 through March 31, 1996

**Objective**

This project focused on the synthesis and characterization of water soluble and/or water-borne electrically conducting polymer systems that could be cross-linked thermally or photochemically. The development of these materials was carried out so that they could be applied as metal and fabric coatings. Polyaniline, polypyrrole, and polythiophene were the polymers under investigation. The main impediment preventing commercial development of these polymers is their inherent insolubility. Methods employed to enhance polymer solubility were monomer or polymer modifications.

The post-polymerization modifications were derivatizations of the parent polymers that involved attachment of suitable pendant groups that would enhance polar solvent solubility. The pendant groups of these derivatized polymers were then further reacted to cross-link, rendering the polymer insoluble. The other modifications involved polymerization of monomers in the presence of polyelectrolytic polymers. The acid functionalities of the electrolyte served as a template/dopant for monomer alignment/complexation before polymerization, resulting in a water soluble (or water borne) composite or complex.

**Modification of Polymers**

Polythiophene, polyaniline, and polypyrrole were used in this phase of the project. After isolation and dedoping, they were chlorosulfonated by refluxing with chlorosulfonic acid. This facilitated further derivatization via nucleophilic substitution. Although chlorosulfonation was carried out successfully at lower temperatures and characterized with IR spectroscopy, solubility enhancement was afforded only with elevated reaction temperatures. The soluble samples were found to have a significant degree of polymer degradation through ring opening upon analysis with  $^1\text{H-NMR}$ . Derivatization of polythiophene sulfonyl chloride with 2-aminoethanethiosulfuric acid (AETSA) was successfully characterized with IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopy. This material was soluble in DMSO, DMF, and water. This solubility was lost after the material was cross-linked with heating. The samples of polythiophene and its derivatives all showed very low conductivities, with  $8.5 \times 10^{-4} \text{ S/cm}$  the maximum achieved for ferric chloride doped polythiophene. Polyaniline emeraldine base was also derivatized like the polythiophene mentioned above and characterized with IR and NMR techniques. Because of the polymer degradation encountered with this derivatization method and the inability of thiophene to polymerize in an aqueous environment, this route of achieving solubility was not pursued further.

**Use of Lignosulfonic acid as a Template/Dopant**

Lignosulfonic acids were used as a templates/dopants for the synthesis of polyaniline and polypyrrole. The high solubility of lignosulfonic acids in water and their doping capability made them a candidate for this part of the project. Prior to polymerization of pyrrole and aniline, commercially available lignosulfonates were protonated by passing a solution through a protonated ion exchange medium. The resulting lignosulfonic acid was used in lieu of the HCl commonly used in the polymerization of aniline and pyrrole with ammonium persulfate. In a typical polymerization, the monomer and an aqueous solution of lignosulfonic acid were stirred at  $0^\circ\text{C}$  for one hour followed by the addition of the oxidizer. Polymerization was carried out for three hours at room temperature after adding the oxidizer. The polymer-dopant complexes were precipitated with acetone and dried

under vacuum prior to analysis. Only the polyaniline-lignosulfonic acid complex was soluble when synthesized using this procedure. This particular complex was soluble in DMSO and to a lesser extent in NMP, accompanied by a color change from green to blue. The complexes were water-borne (not water soluble), but DMSO and NMP solutions were miscible in water with a color change from blue to green. The insolubility of the solid doped polyaniline is believed to be an effect of the polymer complex conformation rather than the lack of sufficient hydrophilic character to solubilize the polymer. When DMSO is used as a solvent, it dedopes the polymer by hydrogen bonding to the hydrogen of the protonated imine, thus weakening its doping effect. The polyaniline chain may then relax, and the polymer complex is dedoped and solubilized. When water is introduced, the DMSO forms hydrogen bonds with the water, loosening its hold on the acidic hydrogen. This facilitates the lignosulfonic acid to redope the polyaniline, observed as the return of the green color. However, this solvent incurred color change is only observed when the dopant concentration is low with respect to the polyaniline, having conductivities in the range of  $1 \times 10^{-4}$  S/cm. The blue to green color transition was observed using UV-Vis and  $^1\text{H}$ -NMR spectroscopy. When a large excess of the lignosulfonic acid or other organic acid is present, the polyaniline is water soluble.

Polymerization of aniline and pyrrole using this method in the presence of various fabrics produced anti-static coatings on the fabrics. This anti-static property was measured using an electrostatic meter. The coatings were quite poor on hydrophobic fabrics such as nylon, but able to resist static charge nonetheless.

#### **Use of External Cross-linking Agents**

The use of external cross-linking agents was developed in order to prevent dopant loss on coated fabrics as well as improve adhesion of the conducting polymers. Bisdiazonium salts have been used to crosslink lignins, and were investigated for this application. The first attempt at crosslinking lignosulfonic acid to a fabric was done by diazotization of 1,4-phenylenediamine and reacting it with lignosulfonic acid in the presence of a nylon and polyester fabrics. Aniline was then polymerized atop the coated fabrics, resulting in heavy, waterfast coatings having bulk resistivities of 46.9 and 3.51  $\text{M}\Omega/\text{in}^2$  for polyester and nylon, respectively. Review of the diazotization procedure and other literature revealed that the 1,4-phenylenediamine was only monodiazotized, resulting in a lignosulfonic acid-polyaniline graft copolymer, not a cross-linked lignosulfonic acid. This was due to the difficulty of two diazonium functionalities to reside on the same ring. Next, 4,4'-bisdiazonium-2,2'-biphenyldisulfonic acid was synthesized and characterized with IR and NMR techniques and subsequently reacted with lignosulfonic acid and lignosulfonic acid-conducting polymer complexes. Cross-linked lignosulfonic acid was characterized mainly by the appearance of sharp peaks in the aromatic region of the  $^1\text{H}$ -NMR spectra and also by its reddish color in basic solution which changed to yellow upon acidification. Polyaniline cross-linked to lignosulfonic acid was virtually indistinguishable (spectroscopically) from the regular polyaniline-lignosulfonic acid complex except for an apparent decrease in solubility. Polypyrrole cross-linked to lignosulfonic acid was soluble in DMSO, giving a dark purple solution. This DMSO solution was miscible in water and was characterized with  $^1\text{H}$ -NMR and UV-Vis spectroscopy.

#### **Conclusions**

The use of lignosulfonic acid has shown the ability to increase the solubility of polyaniline and for polypyrrole when used in concert with an external cross-linking agent. The experimental conditions for cross-linking with the bisdiazonium salts did not result in any apparent degradation of the conducting polymers and may be a more viable means of enhancing their solubility than the derivatizations attempted earlier.